Iron-nickel alloy with low thermal expansion coefficient and exceptional mechanical properties.

The present invention relates to an iron-nickel alloy with low thermal expansion coefficient and exceptional mechanical properties.

It is a known fact that iron-based alloys with approximately 36 % nickel have a low thermal expansion coefficient in the temperature range from 20 to 100 °C. These alloys have therefore been used for years where constant lengths are required even under varying temperatures such as in precision instruments, watches or bi-metals. With the development of the color television sets and computer monitors towards ever greater resolution, color fidelity and contrast, even under unfavorable lighting conditions, and in particular in view of the trend toward ever flatter and larger screens, iron-nickel materials are used more and more for shadow masks.

Technical iron-nickel alloys with approximately 36 % nickel have a thermal expansion coefficient between 1.2 and 1.8 x 10^{-6}/K, in the soft-annealed state as indicated in the "Stahl-Eisen Werkstoffblatt" (steel-iron materials journal) (SEW-385, Edition 1991) in the temperature range from 20 to 100 °C such prevailing in conventional screen tubes. Further developed materials with approximately 36 % nickel are also being used in particular for shadow masks and attain low thermal expansion coefficients between 0.6 and 1.2 x 10^{-6}/K in the temperature range from 20 to 100 °C.

For shadow masks pre-stretched in frames, a low-expansion material with better creep resistance than that of alloys used so far is demanded. The

shadow masks and the frame parts for the shadow masks are subjected to a so-called black-annealing process at temperatures up to approximately 580 °C. Thereby a dark iron oxide layer is produced with which a better visual picture quality is achieved.

The iron-based alloy with approximately 36 % nickel used until now achieves a creep resistance A_{80} of approximately 2.6 % under the following test conditions: 1 hour at 580 °C with a load of 138 MPa.

The shadow masks are pre-stressed in vertical direction by means of the vertical frame parts. Until now iron-nickel alloys with approximately 41% nickel were used, these alloys being known as materials for melting metal to glass for example, or for lead frames. The technological characteristics are as follows: The creep resistance A_{80} is approximately 0.5 % measured under the same testing conditions as described previously for the alloy containing 36 % nickel, i.e. 1 hour at 580°C under a load of 138 MPa. The vertical frame parts made of this alloy become more elongated according to a thermal expansion coefficient of approximately 4.8×10^{-6}/K within a temperature range from 20 to 100 °C than the shadow mask made of the iron-nickel alloy with approximately 36 % nickel.

Newly developed materials for horizontal frame parts should have the same low thermal expansion characteristics as the iron-nickel alloy used until now for shadow masks which, in addition to iron and approximately 36 % Ni, essentially only contain residues due t o manufacture in small amounts.

Just as for the shadow masks, materials with a better creep resistance at temperatures up to 580 °C than that of alloys used until now are demanded for the frame parts. The magnitude and the temperature-dependent course of

the expansion coefficients should be nearly identical with those of the materials used until now.

It is furthermore known that suitable additives to iron-nickel alloys can increase hardening. For this e.g. molybdenum and chromium in combination with carbon can be considered. At the same time the permanent elongation limit and strength increase.

However excessive totals of the elements molybdenum, chromium and carbon can raise the thermal expansion coefficients excessively.

As a wire material for overland lines, an iron-nickel alloy became known, containing approximately 38 Ni, 2 % Mo, 0.8 % Cr and 0.25 % C as well as impurities and iron residue resulting from production. In the solution-annealed state these alloys have a thermal expansion coefficient of approximately 4 x 10^{-6}/K between 20 and 100 °C. The tensile strength can reach values above 1000 N/mm^2 in the hardened state.

JP-A 10060528 discloses an invar alloy with the following combination: ≤0.1 % C, 0.35 % Si, ≤1.0 % Mn, 0.015 % P, ≤ 0.005 % S, ≤ 0.3 % Cr, 35-37 % Ni, 0-0.5 % V, 0.01 % Al, 0-1 % Nb, 0-0.005 % B, ≤ 0.005 % N, iron residue as well as impurities resulting from product ion.

JP-A 10017997 describes another invar alloy that is composed as follows (in percentage by weight): 0.015 % - 0.10 % C, ≤ 0.35 % Si, ≤1.0 % Mn, ≤ 0.015 % P, ≤ 0.0010 % S, 0.3 % Cr, 35 - 37 % Ni, 0 - 0.5 % Mo, 0 - 0.05 % V, ≤ 0,01 Al, 0.15 - < 1.0 % Nb, ≤ 0.003 % Ti, ≤0.005 % N, with S being set to ≤ 0.002 % and Ti to 0.05 – 0.2 %. In addition 0.0005 % - 0:005 % B can be added to the alloy. The remainder is iron and impurities resulting from production.

JP-61183443 relates to an alloy with low thermal expansion coefficients, containing the following alloy elements: 25 – 50 % Ni, ≤ 0.30

% C, ≤ 2.0 % Si + Mn, ≤ 10 % of one or several of the elements Al, Cr, Mo, W, V, Nb, Ta, Ti, Zr and Hr, Fe residue as well as impurities resulting from production. This alloy is to be used among other things for parts of electronic tubes, measuring instruments or similar devices.

Finally DE-A 3642205 describes a shadow mask material which consists essentially, in percentage by weight, of ≤ 0.10 % C, ≤ 0.30 % Si, ≤ ≤ 0.30 % Al, 0.1 – 1.0 % Mn, 34 – 38 % Ni, one or several additional elements such as Ti, Zr, B, Mo, Nb, N, P, Cu, V, Mg, Co and W in contents from 0.01 to 1.0 %, iron residue and unavoidable impurities.

It is the object of the present invention to develop a creep-resistant iron-nickel alloy with low thermal expansion so that it may no longer have the disadvantages indicated in the state of the art, may be economical to produce and may be used in many different technical applications.

This object is attained with a creep-resistant and low-expansion iron-nickel alloy containing (in percentage by weight), in addition to 0.008 to 0.12 % C, 0.05 to 0.30 % Mn and 0.05 to 0.30 % Si and 0.2 to 0.9 % Mo and 0.1 to 0.3 % Cr and 0.03 to 0.15 % Nb and max. 0.5 % Co as well as from 36.0 to 36.5 % Ni, the remainder being iron and impurities resulting from production, whereby the alloy has a thermal expansion coefficient < 2.0×10^{-6}/K within a temperature range from 20 to 100 °C.

A preferred alloy contains (in percentage by weight)

0.08 to 0.11 % C

0.15 to 0.25 % Cr

0.10 to 0.20 % Mn

0.10 to 0.15 % Si

0.5 to 0.7 % Mo

0.05 to 0.09 % Nb

max. 0.1 % Co

36.0 to 36.5 % Ni

remainder being iron and impurities resulting from production.

If necessary further elements can be contained by the inventive alloy (in percentage by weight)

max. 0.002 % S

max. 0.01 % Ti

max. 0.2 % Cu

max. 0.010 % P

max. 0.01 % Al

max. 0.003 % Mg.

Several analysis of the inventive alloy have shown that it is possible to realise a thermal expansion coefficient $< 1.6 \times 10^{-6}/K$ in the temperature range from 20 to 100 °C.

The required technological properties for utilization as a material, in particular for vertical frame parts of shadow masks, can be selected by means of the iron-nickel alloy according to the invention, whereby the composition with regard to Ni, Mo, Cr and C contents can be selected so that the desired thermal expansion coefficients and mechanical properties are obtained.

The object of the invention can be used advantageously for the following objects, in addition to frame parts and shadow masks for screens and monitors:

- passive components of thermo-bimetals
- components in laser technology
- lead frames
- components of electron guns, in particular TV tubes

- components for the production, storage and transportation of liquefied gas

Preferred alloys according to the invention are compared below with alloys according to the state of the art with respect to their mechanical properties.

A preferred composition E1 of the alloy according to the invention for utilization as a material for the vertical frame, e.g. for a screen, contains (in percentage by weight) in addition to 36 to 36.5 % Ni, 0.2 to 0.9 % Mo, <0.2 % Cr and in addition 0.08 to 0.12 % C, also max. 0.3 % Mn, max. 0.3 % Si, max. 0.15 % Nb and the usual impurities in very small quantities resulting from the production process. The thermal expansion coefficient of approximately 2.0 x 10^{-6}/K between 20 and 100 °C and the overall temperature-dependent evolution of the expansion coefficients between room temperature and 600 °C are comparable with the value or the evolution of the two-material alloy T2 used until now according to the state of the art which, in addition to iron and approximately 36 % Ni, only contains impurities resulting from the production process. The improvement of the mechanical properties necessary for the application is achieved with the alloy according to the invention, in particular insofar as the creep-resistance, measured on a 1.4 mm thick cold-rolled sample as extension A80 at 580 °C and this even with a greater load of 200 MPa for one hour, in other words approximately 0.02%. The alloy E1 according to the invention excels through its outstanding workability and requires no additional process steps in production. This means that to obtain the especially good mechanical characteristics, no additional hardening/heating treatment is needed, such as would be needed for example with γ'- precipitation hardenable alloys. The frame can be bent into shape directly in the cold-rolled state. The mechanical

properties as described above are present in this state. In addition the long-term stability of its thermal properties meets all requirements.

Another preferred composition E2 of the alloy according to the invention for application as material for a vertical frame, e.g. of a monitor, contains (in % by weight) in addition to 36 to 36.5 % Ni, 0.4 to 0.8% Mo, 0.1 to 0.3 % Cr and in addition 0.08 to 0.12% C as well as max. 0.3% Mn, max. 0.3% Si, max. 0.15% Nb and the usual impurities resulting from the production process in only very small amounts. The thermal expansion coefficient between 20 and 100 °C at approximately 1.8 x 10^{-6}/K is lower than in the case of the alloy E1 according to the invention. The improvement of the mechanical properties required for the application is also attained with the alloy E2 according to the invention, in particular insofar as the creep-resistance, measured as extension A80 at 580 °C on a cold-rolled sample of 1.4 mm thickness is expressed by a value of approximately 0.03%, even with a load of 200 MPa during one hour. The alloy E2 according to the invention is also remarkable through its outstanding workability and requires no additional process steps in production. This means that in order to obtain the especially good mechanical properties, no additional hardening/heating treatment is needed. The frame can be bent into shape directly in the cold-rolled state. The mechanical properties as described above are present in this state. In addition the long-term stability of its thermal properties meets all requirements.

The required technological properties for utilization as a material, in particular for vertical frame parts for shadow masks can be obtained with the iron- nickel alloy according to the invention, whereby the composition with

regard to Ni, Mo, Cr, Nb and C contents can be selected so that the desired thermal expansion coefficients and mechanical properties are present.

The mechanical properties that were determined in a hot-drawing test without load at the testing temperature of 580 °C as well as the magnetic coercitive field force as well as the thermal expansion coefficients are shown in Table 1 for the alloys E1 and E2 according to the invention as compared with the properties of the alloys T1 and T2 of the state of the art.

Element	E1	E2	T1	T2
Hot drawing test at 580 °C				
Permanent elongation limit				
$Rp_{0.005}$ (N/mm^2)			189	261
$Rp_{0.1}$ (N/mm^2	323	347		
$Rp_{0.2.}$ (N/mm^2	460	438	312	322
Tensile strength				
R_m (N/mm^2)	485	451	411	381
Elongation at rupture				
A_{80} (%)	3.80	4.40	7.5	6.4
Creep resistance				
load 200 N/mm^2	200 N/mm^2		138 N/mm^2	
	0.02	0.03	0.54	2.61

Thermal expansion coefficients (from 20 °C to testing temperature T in 10^{-6}/K)

T (°C)				
100	2.0	1.8	4.88	1.26
200	2.6	2.6	4.49	2.45
300	5.2	5.3	4.52	5.47
400	8.1	8.2	6.31	8.28
500	10.0	10.2	8.14	10.23
600	11.4	11.6	9.69	11.61

Table 1: Mechanical characteristics permanent elongation limit, tensile strength, elongation to rupture at 580 °C, determined in hot drawing test, as well as creep resistance for 1 hour at 580 °C with a load of 138 MPa or 200 MPa and the thermal expansion coefficients of the alloys E1 and E2 according to the invention as compared with the alloys T1 and T2 of the

state of the art. The testing sample was made from a 1.4 mm cold-rolled band.

Examples of the chemical composition of the alloys E1 and E2 according to the invention as compared with the composition of the alloys T1 and T2 of the state of the art are listed in Table 2.

Element (% by mass)	E1	E2	T1	T2
C	0.108	0.109	0.007	0.003
S	0.0008	0.0008	0.003	0.0003
N	0.001	0.001	0.002	0.0025
Cr	0.015	0.20	0.03	0.03
Ni	36.40	36.40	40.80	36.15
Mn	0.13	0.14	0.55	0.24
Si	0.10	0.10	0.17	0.06
Mo	0.70	0.62	0.01	0.05
Ti	0.01	0.01	0.005	<0.01
Nb	0.05	0.05	<0.01	0.01
Cu	0.01	0.01	0.04	0.05
Fe	Remainder			
P	0.002	0.002	0.003	0.002
Al	0.005	0.001	0.002	0.007
Mg	0.001	<0.001	<0.001	0.002
Co	0.01	0.01	0.04	0.04
O	0.0055	0.0055	0.002	0.002

Table 2: Examples of chemical compositions of the alloys E1 and E2 according to the invention as compared with examples of compositions of alloys T1 and T2 of the state of the art.

For certain fields of application it may be advisable to add cobalt in the indicated amounts (in % by weight) of the alloy according to the invention. Preferred additions of cobalt (in % by weight) are between 0.1 and 0.5%, whereby the nickel content must then be adjusted correspondingly.